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(54) Title: ULTRAMULSION BASED PAINT AND COATING PRODUCTS (57) Abstract <p>The present invention relates to various paint and coating products containing, stable, dispersions of certain high viscosity silicones in certain surfactants; wherein: said dispersions are free from VOCs and HAPs and: a. the dispersed silicones, which are insoluble in said surfactant, are oriented by the surfactant such that when dispersed in water they are particularly adept at forming oriented coatings on substrates enhanced substantivity, and b. the particle size of the dispersed silicone is from between about 0.5 and about 10 microns, with a particle size distribution such that from between about 80 and 95 % of the dispersed silicone is within this particle size range. These stable dispersions are described as ULTRAMULSION™ dispersions, which, together with their physical properties, when contained in paint and coating products, provide these products with distinctive weathering, water repellency, etc. properties where the non continuous, high viscosity, silicone phase contributes to enhanced substantivity of said paints and coatings to various substrates.</p>		

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ULTRAMULSION BASED PAINT AND COATING PRODUCTS

BACKGROUND OF THE INVENTION

The present invention relates to unique paint and coating compositions containing a dispersion of certain silicones in certain surfactants wherein said dispersions are free from volatile organic chemicals (VOCs) and free from hazardous air pollutants (HAP). When added to water based paints and coatings these dispersions are stable and are distinct from solutions, emulsions and microemulsions. These dispersions are referred to hereinafter as ULTRAMULSION™ dispersions. This trademark is the property of Whitehill Oral Technologies, Inc.

The ULTRAMULSION™ dispersion based paint and coating products of the present invention exhibit antifoam and wetting properties along with unique and unexpected substantivity to various surfaces resulting in improved weatherability and the ability to seal certain surfaces from water penetration.

U.S. Government restrictions relating to volatile organic compounds (VOCs) and to hazardous air pollutants (HAPs) under the Clean Air Act of 1990, suggest that the water dispersible, solvent free NO VOC, NO HAP ULTRAMULSION™ dispersions of the present invention are excellent alternatives to the current VOC and HAP solvent based silicones used as antifoam and wetting flow control agents in commercial paint and coating products.

Heretofore solvent based silicones have been attractive high performance additives for paints and coatings based on their contributions to mar resistance, adhesion and water resistance while functioning as leveling agents and wetting paint off the brush while preventing foaming. But their VOC and HAP content can no longer be accepted and reformulation is called for. See *Chemical and Engineering News*, p. 44-66, (Oct 3 1994). Existing and pending limits on VOCs and HAP are

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forcing most paint and coatings makers to reformulate many of their lines to comply with regional and national rules limiting VOCs and HAP in architectural and maintenance coatings.

5 The ULTRAMULSION™ dispersions of the present invention contribute wetting, leveling, antifoaming, etc., properties to various paints and coatings while introducing no VOC, no HAP to these products. In addition, the enhanced substantivity of these ULTRAMULSION™ dispersions to the substrate being painted or coated imparts unobvious and unexpected improvements in adhesion, weatherability, water resistance and the like to these paintings and coatings.

10 Silicones in various compositions have been disclosed in a number of different publications. Such publications include U.S. Pat. No. 2,826,511, March 11, 1958 to Green; U.S. Pat. No. 3,964,500, June 22, 1976 to Drakoff; U.S. Pat. No. 4,364,817, December 21, 1982 to Pader; and British Pat. No. 849,433, September 28, 1960 to Woolston. While these patents disclose silicone containing
15 compositions, they also do not provide answers to all of the problems encountered in making a totally satisfactory paint or coating product. One problem is that of keeping a dispersed, insoluble silicone material suspended and the total product stable.

20 The ULTRAMULSION™ dispersions of the present invention are distinct from other emulsions as will become apparent from the following background:

When a system consists of a single liquid phase it is described as a solution. A system containing two or more liquid phases is described as a multiphase solution or emulsion. According to Becher, an emulsion is an unstable heterogeneous system in which the diameters of the dispersed droplets in general exceed 1000Å.
25 Becher P. in "Emulsions, Theory and Practice," (P. Becher, Ed.) page 2, Rheinhold, New York, 1965. A more comprehensive definition of emulsion is advanced by Clayton: "An emulsion is a system containing two liquid phases, one of which is dispersed as globules in the other. The liquid which is broken up into globules is termed the dispersed or discontinuous phase, while the liquid surrounding the
30 globules is known as the continuous phase or dispersing medium" Clayton, W., "The Theory of Emulsions and Their Technical Treatment," 4th Ed. page 1, the Blakiston Co., Philadelphia, 1943. It is well accepted that, mechanical work is

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required to effect such an emulsion, see Bancroft W. D., *J. Phys. Phy. Chem.*, 17: 501 (1913). According to Prince, an emulsion may be defined as a dispersion of two (or more) mutually insoluble liquids, one in the other. Because of the surface tension forces at play between the two liquids, the dispersed phase consists of spherical droplets. Prince, L.M. in "Microemulsion Theory and Practice," pg. 2, Academic Press Inc., New York, NY (1977). See also Prince, L.M. in "Biological Horizons in Surface Science," pg. 361, Academic Press Inc. (1973).

Emulsions, are generally not stable and upon standing or after centrifuging tend to separate into two or more liquid layers. The three definitions of emulsions set forth above share one common attribute, that is, mechanical work must be put into the emulsions described in order to disperse one liquid in the other in the form of droplets. This mechanical work can be in the form of agitation, homogenization, ultrasonication, etc.

In contrast, dispersions of very small droplet sizes which are formed spontaneously without the input of any mechanical work are called microemulsions. See Prince 1977, p. 3. Generally, two surfactants are used in forming microemulsions, i.e., a water soluble surfactant and a co-surfactant such as alcohol, where one phase of the microemulsion is generally water. Thus, dilution or adulteration of the dispersed phase by the co-solvent generally accompanies microemulsion formation. The ratio of surfactant to dispersed phase in microemulsions is much higher than that of emulsions. Microemulsions are further characterized as optically clear or opalescent and when spun in a laboratory centrifuge for 5 minutes at 100 G's, the dispersion remains stable and does not separate. Thus, fine particle sizes, exceptional stability and rheological properties that can be easily adjusted, distinguish microemulsions from emulsions. Moreover, to date, no microemulsions have appeared in which one of the mutually insoluble liquids is not water. See Prince, page 34, (1977).

It has been surprisingly found that certain ULTRAMULSION™ dispersions i.e., those of the present invention, provide various paint and coating products with the requisite wetting, antifoam, flow adjusting properties along with unexpected improvements in adhesion, bonding, waterproofing, etc., with these latter attributed to their enhanced substantivity and the reservoir effect achieved by solubilizing

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various lipid soluble adhesion enhancing substances in the discontinuous silicone phase of the ULTRAMULSION™ dispersion.

SUMMARY OF THE INVENTION

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The ULTRAMULSION™ dispersions of paint and coating products of the present invention combine certain characteristics of emulsions with certain features of microemulsions. That is, like emulsions, they are two phase systems comprising a silicone dispersed in a continuous, surfactant phase, wherein the silicone is
10 insoluble in the surfactant. Unlike emulsions, but like microemulsions, these dispersions are stable. Unlike microemulsions, but like emulsions, mechanical work is required to form ULTRAMULSION™ dispersions. Like microemulsions, but unlike emulsions, these ULTRAMULSION™ dispersions are not formed spontaneously. Like emulsions, the ULTRAMULSION™ dispersions do not
15 contain a cosolvent commonly found in microemulsions. Of course, the ULTRAMULSION™ dispersions of the present invention can be dispersed in various liquids such as water as stable dispersions. These dispersions of ULTRAMULSION™ dispersions in water have excellent utility in various paint and coating products. See various examples below.

20

While not wishing to be bound by theory, it is hypothesized that unlike either emulsions or microemulsions, the dispersed silicones of the ULTRAMULSION™ dispersions of the present invention are oriented with their polar moieties in one general plane and their hydrophilic moieties in a plane approximately opposite that of the polar moieties. This orientation promotes
25 stability as well as bonding between the polar or hydrophilic moieties and various substrates thereby effecting oriented, monolayer coatings of the silicone. These oriented dispersions of silicones have a broad range of utility in painting and coating as detailed in the various examples below.

30

The emulsifying effects of uncoiling of the silicone molecule with the oxygen moieties generally oriented in one plane distinct from that of the organo moieties as illustrated in Figs 1 and 2 are further substantiated by the following references: *Eur. Poly. J.*, 26: 654 (1990); *J. Chem. Phys.*, 49: 1398 (1965); *J.*

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Chem. Phys., 54: 5011 (1971); *J. Chem. Phys.*, 59: 3825 (1973); *Macromolecules*, 7: 229 (1974); *Macromolecules*, 11: 627 (1978) and "Rubber-Like Elasticity: A Molecular Primer," J. Mark, New York, Wiley-Interscience (1988).

5 Methods of preparing polyorganosiloxane emulsions with an average particle size of less than about 0.3 microns and polyorgano-siloxane microemulsions with an average particle size of less than about 0.14 micron are described in U.S. Pat. No. 4,620,878. Preparation of oil-in-water microemulsions are described in U.S. Pat. No. 4,146,499. Specific surface active compositions used as emulsifiers with diorganopolysiloxanes to form transparent microemulsions are described in U.S. Pat. 10 Nos. 4,0562,331 and 3,975,294. U.S. Pat. No. 3,433,780 teaches the preparation of colloid silane suspensions. See also "Chemistry and Technology of Silicones," W. Noll, pp. 428 to 431 (1968); *Journal of Society of Cosmetic Chemists*, 25: 609-619 (1974) and *Journal of Colloid and Interface Science*, 44: 242-248 (1973).

15 Micellar dispersions, microemulsions, and transparent emulsions are described in detail in "Annals of the New York Academy of Science," Shulman and Montagne (1961); U.S. Pat. No. 2,356,205, "The Theory of Emulsions and Their Technical Treatment," 5th Edition, 1954, U.S. Pat. Nos. 3,497,006; 3,506,070, 3,254,714 and 3,307,628.

For the purposes of the present invention:

- 20 a. "Stable" refers to the stability of a dispersion of the ULTRAMULSION™ dispersion in water, whereby when subjected to centrifuging in a 100 G environment for 5 minutes, less than about 10% by weight of the ULTRAMULSION™ dispersion separates from the continuous water phase.
- b. "Water-free" means that the ULTRAMULSION™ dispersion of silicone and 25 surfactant is substantially free from water.
- c. "Solvent free" means that the ULTRAMULSION™ dispersion of silicone and surfactant is substantially free from co-solvents such as ethanol, isopropanol, etc. and from typical VOC and HAP solvents used with silicone in paints and coatings.
- 30 d. "Oriented" means that the polar moieties of the "uncoiled" polydimethylsiloxane in the ULTRAMULSION™ dispersion are generally aligned in one plane with the hydrophilic oil seeking moieties aligned in a second plane

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such as illustrated in Fig. 2.

e. "Monolayer" means that the monomolecular film of the ULTRAMULSION™ dispersion of the invention when dispersed in water is attracted to the substance of interest by secondary bonding force to form a substantive coating thereon.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates the "coiled" molecular configuration of polydimethylsiloxanes;

Fig. 2 illustrates the molecular configuration of oriented polydimethylsiloxanes after ULTRAMULSION™ dispersion processing;

Fig. 3 illustrates schematically an ULTRAMULSION™ dispersion process of the invention; and

Figs. 4 and 5 illustrate that the ULTRAMULSION™ dispersions of the invention produced via various high shear dispersing means having particle size distribution of 80+ % under 10 microns.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to the drawings, Fig. 1 illustrates the accepted "coiled" configuration advanced for polydimethylsiloxanes, wherein the methyl moieties are oriented outward while the oxygen moieties are oriented inward towards the axis of the coil or helix. This configuration does not readily promote "bonding" between the oxygen moieties and compatible surfaces.

Fig. 2 illustrates the "uncoiled oriented" configuration proposed for polydimethylsiloxanes that have been dispersed in the stable, ULTRAMULSION™ dispersions of the present invention, wherein the oxygen moieties are generally oriented in one plane distinct from that of the methyl moieties. This proposed uncoiled oriented configuration appears to support the unique and unexpected "bonding" and enhanced substantivity properties of the ULTRAMULSION™ dispersions of the present invention, as evidenced by the various improved painting

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and coating applications of these ULTRAMULSION™ dispersions. See examples below.

Fig. 3 illustrates the ULTRAMULSION™ dispersion process of the present invention wherein a surfactant and a polydimethylsiloxane 1, substantially free from water and co-solvent, are mixed in vessel 2, provided with mixing means 3, heat source 4, and inert head space 5. The heated and mixed surfactant - polydimethylsiloxane 6, is then subjected to high shear dispersion at an elevated temperature in dispersing means 7, to produce the ULTRAMULSION™ dispersion 8, of the invention. These ULTRAMULSION™ dispersions are VOC and HAP free.

Fig. 4 is a chart describing the typical particle size distribution of an ULTRAMULSION™ dispersion of the present invention containing from about 50 to 95% by weight nonionic surfactant and from about 5 to 50% by weight polydimethylsiloxane (2.5 million cs) produced in a continuous process with an IKA Works dispersing means, (high shear dispersing) with an inlet temperature of 140°C and an outlet temperature of 210°C.

Fig. 5 is a chart describing the typical particle size distribution of an ULTRAMULSION™ dispersion of the present invention containing from about 50 to 95% by weight nonionic surfactant and from about 5 to 50% by weight polydimethylsiloxane (2.5 million cs) produced in a batch process with a Ross M/E 100 LC dispersing means fitted with a 20 mesh screen, operated at a temperature from about 120° to 160°C.

For purposes of the present invention, "silicone" means a clear, colorless substance coating polyalkylsiloxane polymers with average kinematic viscosities up to 4 million cs. These high viscosity polydimethylsiloxanes having viscosities from about 2.5 million cs to about 4 million cs are particularly preferred for the paint and coating products, of the present invention. Other polydimethylsiloxanes suitable for the present invention are described in various product brochures published by Dow Corning Corporation, Midland, Michigan. See also Tables 2 and 3 below. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970.

The silicone fluid may be either a high viscosity polyalkyl siloxane as described in detail below, a polyaryl siloxane, a polyalkylaryl siloxane or a

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polyether siloxane copolymer. Mixtures of these silicones may also be used and are preferred in certain embodiments of the present invention.

The polyalkylaryl siloxanes that may be used include, for example, polymethylphenylsiloxanes having viscosities above 1 million centistokes at 20°C.
5 Some of these siloxanes are available, for example, from the General Electric Company.

The polyether siloxane copolymer that may be used is, for example, a polypropylene oxide modified dimethylpolysiloxane although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used.

10 References disclosing suitable silicone fluids include U.S. Pat. No. 2,826,551 to Green; U.S. Pat. No. 3,964,500 to Drakoff; U.S. Pat. No. 4,364,837 to Padner and British Pat. No. 849,433 to Woolston. See also, "Silicon Compounds" distributed by Petrarch Systems, Inc., 1984. This reference provides a very good listing of suitable silicone materials.

15 Silicone materials found especially useful in the present compositions to provide good leveling etc and enhanced substantivity gums are silicone gums. Silicone gums are described by Petrarch and others including U.S. Pat. No. 4,152,416, May 1, 1979 to Spitzer et al., and Noll, Walter, "Chemistry and Technology of Silicones," New York: Academic Press 1968. Also describing
20 silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. "Silicone gum" materials denote high molecular weight polydiorganosiloxanes having a mass molecular weight of from about 200,000 to about 4,000,000. Specific examples include polydimethylsiloxane, (polydimethylsiloxane)-(methylvinylsiloxane), copolymer, poly(dimethylsiloxane)-
25 (diphenyl)(methylvinylsiloxane) copolymer and mixtures thereof.

High viscosity polydimethylsiloxanes are particularly preferred. The safety of polydimethylsiloxanes for use in these various products is well documented. See Rowe et al., *Journal of Industrial Hygiene*, 30(6): 332-352 (1948). See also Calandra et al., *ACS Polymer Preprints*, 17: 1-4 (1976) and Kennedy et al., *J. Toxicol. and Environmental Health*, 1: 909-920 (1976).
30

As noted above, the preferred polydimethylsiloxanes useful in the paint and coating compositions of the present invention are described as

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polydimethylsiloxanes with the chemical formula



5 wherein n is a whole number. These polydimethylsiloxanes have viscosities ranging from between about 2.4 million and about 4 million cs. and are generally described as having molecular weights between about 2.5 million and several million.

The particle size of the silicone in the ULTRAMULSION™ dispersions of the present invention can range from between about 0.5 and about 10 microns. In a
 10 preferred embodiment of the present invention the particle size of polydimethylsiloxanes in the ULTRAMULSION™ dispersion ranges from between about 1 and about 5 microns. The particle size distribution of the polydimethylsiloxanes in the ULTRAMULSION™ dispersions of the present invention generally range from between about 80 and about 95% of the particles
 15 under 10 microns. See Figs. 4 and 5. In a preferred embodiment of the present invention, from between about 80 and about 95% of the particles are under 5 microns. See also Table 3.

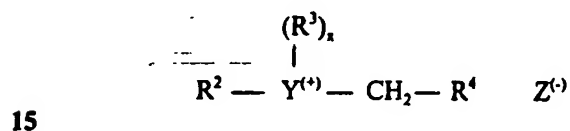
An essential component of the ULTRAMULSION™ dispersion is a surfactant. The surfactant, may be selected from any of a wide variety of synthetic
 20 anionic, amphoteric, zwitterionic and nonionic surfactants.

Synthetic anionic surfactants can be exemplified by the alkali metal salts of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from 8-22 carbon atoms and a sulfonic acid or sulfuric acid ester radical (included in the term alkyl is the alkyl portion of higher acyl radicals).
 25 Preferred are the sodium, ammonium, potassium or triethanolamine alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8 - C_{18} carbon atoms), sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of 1 mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and 1 to 12 moles of ethylene
 30 oxide ether sulfate with 1 to 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to 12 carbon atoms, sodium alkyl glyceryl ether sulfonates; the reaction product of fatty acids having from 10 to 22 carbon atoms

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esterified with isethionic acid and neutralized with sodium hydroxide; water soluble salts of condensation products of fatty acids with sarcosine; and other known in the art.

Zwitterionic surfactants can be exemplified by those which can be broadly
 5 described as derivatives of aliphatic quaternary ammonium, phosphonium, and
 sulfonium compounds, in which the aliphatic radicals can be straight chain or
 branched, and wherein one of the aliphatic substituents contains from about 8 to 18
 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxyl,
 sulfonate, sulfate, phosphate, or phosphonate. A general formula for these
 10 compounds is:



wherein R^2 contains an alkyl, alkenyl, or hydroxyl alkyl radical of from about 8 to
 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1
 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorous,
 20 and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing 1 to about 3
 carbon atoms; X is 1 when Y is a sulfur atom and 2 when Y is a nitrogen or
 phosphorous atom; R^4 is an alkylene or hydroxyalkylene of from 1 to about 4
 carbon atoms and Z is a radical selected from the group consisting of carboxylate,
 sulfonate, sulfate, phosphonate, and phosphate groups. Examples include; 4-[N,N-
 25 di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate; 5-(S-3-
 hydroxypropyl-S-hexadecylsulfonio)-3-hydroxypentane-1-sulfate; 3-[P,P-diethyl-P-
 3,6,9-trioxatetradecocylphosphonio]-2-hydroxypropane-1-phosphate; 3-[N,N-
 dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphate; 3-[N,N-
 dimethyl-N-hexadecylammonio-propane-1-sulfonate; 4-[N,N-di(2-hydroxy-ethyl)-N-
 30 (2-hydroxydodecyl)ammonio]-butane-1-carboxylate; 3-[S-ethyl-S-(3-dodecoxy-2-
 hydroxypropyl)sulfonio]-propane-1-phosphate; 3-[P,P-dimethyl-P-dodecyl-
 phosphonio]-propane-1-phosphonate; and 5-(N,N-di(3-hydroxypropyl)-N-
 hexadecylammonio)-2-hydroxypentane-1-sulfate.

Other zwitterionics such as betaines are also useful in the present invention.

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Examples of betaines useful herein include the higher alkyl betaines such as cocodimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha-carboxyethylene betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxy-ethyl)carboxy methyl betaine, stearyl bis-(20-hydroxy-propyl)-
5 carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine, etc. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxy-ethyl)sulfopropyl betaine and the like; amido betaines and amidosulfo betaines, wherein the
10 $\text{RCONH}(\text{CH}_2)_3$ radical is attached to the nitrogen atom of the betaine are also useful in this invention.

Examples of amphoteric surfactants which can be used in the ULTRAMULSION™ dispersions of the present invention are those which can be broadly described as derivatives of aliphatic secondary and tertiary amine in which
15 the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecylamino-propionate, sodium 3-dodecylamino-propane sulfonate,
20 N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Pat. No. 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Pat. No. 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Pat. No. 2,528,378.

25 Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic surfactants are:

30 1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with

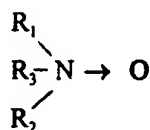
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ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, disobutylene, octane, or nonane, for example.

5 2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing
10 from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000 are satisfactory.

15 3. The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

20 4. Long chain tertiary amine oxides corresponding to the following general formula:



25 wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms from 0 to about 10 ethylene oxide moieties, and from 0 to 1 glyceryl moiety, and R_2 and R_3 contains from 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxy ethyl, or hydroxypropyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Example of amine oxides suitable for use in this invention
30 include dimethyl-dodecylamine oxide, oleyldi(2-hydroxy-ethyl)amine oxide, dimethyloctylamine oxide, dimethyl-decylamine oxide, dimethyltetradecylamine oxide, 3,6,9-trioxaheptadecyl-diethylamine oxide, di(2-hydroxyethyl)-tetracyclamine

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oxide, 2-dodecoxyethyl dimethylamine oxide, 3-dodecoxy-2-hydroxypropyl di-(3-hydroxy-propyl)amine oxide, dimethylhexadecylamine oxide.

5. Long chain tertiary phosphine oxides corresponding to the following general formula:



wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from 8 to 18 carbon atoms in chain length from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are: dodecyl dimethyl phosphine oxide, tetradecyl dimethyl phosphine oxide, tetradecyl methyl ethyl phosphine oxide, 3,6,9-trioxaocta-decyl dimethyl phosphine oxide, cetyl dimethyl phosphine oxide, 3-dodecoxy-2-hydroxypropyl di-(2-hydroxy)-phosphine oxide, stearyl dimethyl phosphine oxide, cetyl ethyl propyl phosphine oxide, cetyl diethyl phosphine oxide, dodecyl diethyl phosphine oxide, tetradecyl diethyl phosphine oxide, dodecyl dipropyl phosphine oxide, dodecyl di(2-hydroxyethyl)-phosphine oxide, tetradecyl methyl-2-hydroxydodecyl dimethyl-phosphine oxide.

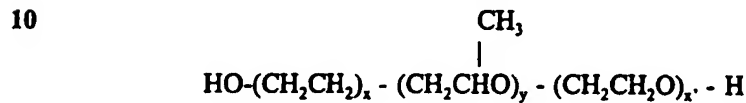
6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of 1 to about 3 carbon atoms (usually methyl) and one long hydrophosphic chain which contain alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety. Examples include: octadecyl menthyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-trioxsoctadecyl 2-hydroxyethyl sulfoxide, dodecyl menthyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl menthyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxy-butyl methyl sulfoxide. Many additional nonsoap surfactants are described in McCUTCHEON'S, DETERGENTS AND EMULSIFIERS, 1979 ANNUAL, published by Allured Publishing Corporation.

The nonionic surfactants most useful in the present invention are nonionic

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surfactants of block copolymers of ethylene oxide and propylene oxide ranging from flowable liquids of varying viscosities, to paste, prills and cast solids with molecular weights from 1,100 to 150,000. Suitable nonionic surfactants are manufactured and marketed by BASF Corporation under the trademarks Pluronic.

5 Particularly preferred nonionic surfactants are Pluronic F-68, F-88, F-108 and Pluronic F-127. These are described in a BASF brochure entitled "Pluronic and Tetronic Block Copolymer Surfactant." These nonionic surfactants suitable for the present invention can be described by the following structure:



15 where x, y and x' are whole numbers. Surprisingly, the nonionic surfactants of choice for the ULTRAMULSION™ dispersions of the present invention are reported in the referenced brochure to have marginal detergency, emulsification and wetting properties. See Tables 2 and 3.

As noted above, the nonionic poloxamer surfactants useful in the paint and
20 coating compositions of the present invention are described as polyoxyethylene-polyoxypropylene block copolymers such as Pluronic F-68, F-88, F-108 and F-127 (BASF) which have molecular weights of at least about 1000 such as described in U.S. Pat. Nos. 4,343,785, 4,465,663, 4,511,563 and 4,476,107.

Emulsions of various coating substances including polydimethylsiloxanes in
25 various surfactants including nonionic surfactants are disclosed and claimed in U.S. Pat. Nos. 4,911,927, 4,942,034; 4,950,479; 5,009,881; 5,032,387; 5,057,306; 5,057,307; 5,057,308, 5,057,309; 5,057,310, 5,098,711, 5,165,913 and 5,284,648. There is no teaching in these references that these high viscosity silicone emulsions are stable nor that the silicones are oriented as they are in the ULTRAMULSION™
30 dispersions of the present invention.

The ratio of surfactant to silicone in the ULTRAMULSION™ dispersions of the present invention can range from between about 400:1 and about 1:2. In a preferred embodiment of the invention the ratio of surfactant to silicone is from between about 25:1 and 1:2.

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The ULTRAMULSION™ dispersions of the present invention are prepared as follows; generally, if not a liquid, the surfactant is heated to a temperature at which it becomes a liquid. The silicone is dispersed in the heated surfactant with various high shear dispersing means.

5 Specifically the heated surfactant is mechanically stirred along with the silicone. This mixture is subjected to high-shear dispersions with a means such as the IKA-WORKS DISPAX-Reactor with at least one superfine generator, alternatively, a Ross Model M.E., 100 LC fitted with a 20 mesh screen or a
10 ultrasonicator such as MEDSONIC XL2010 fitted with 800-C Flow Cell and 800-21CT 3/4 inch flanged horn can be used.

 Various ULTRAMULSION™ dispersions which are prepared and analyzed are described in detail in the examples below. Specific poloxamer-polydimethyl-siloxane ULTRAMULSION™ dispersions suitable for use with various paint and coating products were prepared as described in Table 1 below:

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TABLE 1

	% W/W					
Example	1	2	3	4	5	6
COMPONENT						
Dimethicone						
viscosity (centistokes)						
2,500,000 (cs)	10	-	33	-	20	-
4,000,000 (cs)	-	10	-	33	-	20
Poloxamer-188	-	-	-	-	80	-
Poloxamer-238	-	-	-	-	-	80
Poloxamer-338	90	90	-	-	-	-
Poloxamer-407	-	-	67	67	-	-

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PROCEDURE

The Poloxamer is heated to 70-90°C to melt the solid material. Once melted the Poloxamer is stirred with an overhead mixing blade. Dimethicone is added and the entire mass is mixed to obtain a uniform dispersion while
5 maintaining temperature. The material is then transferred to the homogenizer, ROSS homogenizer, model M.E. 100LC, and homogenized for 1 hour at 10,000 RPM. The material is then cooled by a suitable cooling apparatus. The cooled material is then ready for use.

Specific Poloxamer/polydimethylsiloxane ULTRAMULSION™ dispersions
10 suitable for use with various paint and/or coating products were prepared and analyzed as described in Tables 2 and 3 below.

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TABLE 2
PARTICLE SIZE DISTRIBUTION (%)

Example No.	Product Composition (w/w)	<1 μ	<2 μ	<3 μ	<4 μ	<5 μ	>10 μ
7	67/33 Poloxamer 338 and 100,000 cs. Dimethicone	44	50	4	1	1.0	0
8	90/10 Poloxamer 338 and 600,000 cs. Dimethicone	24	4	5	1	2	0
9	90/10 Poloxamer 407 and 2,500,000 cs. Dimethicone	2	3	63	24	8	0
10	90/10 Poloxamer 407 and 4,000,000 cs. Dimethicone	1.5	6	.51	43.5	14	0

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TABLE 3
PARTICLE SIZE DISTRIBUTION (%)

Example No.	Product Composition (w/w)	0-2 μ	2-4 μ	5-10 μ	>10 μ
11	90/10 Poloxamer 338 and 2,500,000 cs. Dimethicone	13.0	85.7	1.3	0
12	90/10 Poloxamer 338 and 4,000,000 cs. Dimethicone	8.67	77.08	14.25	0
13	67/33 Poloxamer 407 and 2,500,000 cs. Dimethicone	15.0	84.5	0.5	0
14	80/20 Poloxamer 188 and 2,500,000 cs. Dimethicone	3.4	83.75	12.85	0
15	80/20 Poloxamer 238 and 4,000,000 cs. Dimethicone	1.7	78.6	19.7	0

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The discontinuous silicone phase of the ULTRAMULSION™ dispersion can also contain a wide range of lipid soluble and/or lipid dispersible ingredients to impart certain properties of the final film coating. These various ingredients in the silicone phase of the ULTRAMULSION™ dispersion perform as though they are contained in a "reservoir" as they continue to be available at the ULTRAMULSION™ dispersion containing - substrate interface, as long as the ULTRAMULSION™ dispersion coating remains substantive to the substrate. The sustained effect - i.e., improved weatherability, resistance to water, etc. obtained with these improved paint and coating products are discussed in various examples below.

The paint and coating products containing the ULTRAMULSION™ dispersions of the present invention can also contain a variety of other essential components. These are detailed in various Examples described below.

For example, water is an essential component of most low VOC, low HAP paint and coatings of the present invention which contain one or more of the various ULTRAMULSION™ dispersions described above. The water in these products is generally present at a level of from about 20% to about 95%, preferably from between about 60% and about 90%.

In addition these paint and coating products can contain a variety of nonessential optional components suitable for rendering such compositions more acceptable. See the Examples provided below. The paint and coating products of the present invention can be made by mixing the materials together and heating to between about 70°C and 90°C. The mixture is mixed thoroughly for about 10 minutes at between about 70°C and 90°C before being pumped through a heat exchanger to cool it to ambient temperature.

The following Examples further describe and demonstrate preferred embodiments within the scope of the present invention. The Examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention as many variations thereof are possible without departing from its spirit and scope.

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TABLE 4

% W/W

Example No.	16	17
Component:		
TEA C ₁₂ -C ₁₄ Alkyl Sulfate	15.0	---
NH ₄ C ₁₂ -C ₁₄ Alkyl Ether Sulfate	---	1.90
Sodium C ₁₂ -C ₁₄ Alkyl Sulfate	---	1.90
Cocamide MEA	3.00	1.50
ULTRAMULSION:		
Example 3	3.00	---
Example 4	---	3.00
Cocoamidopropyl Betaine	1.50	1.50
Citric Acid	0.60	0.60
Sodium Chloride	0.40	0.40
Color/Preservative/Fragrance	qv	qv
D.I. Water	-----qv to 100%-----	

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TABLE 5

EXAMPLE	% W/W					
	18	19	20	21	22	23
Component						
Ammonium Lauryl Sulfate	12.0	12.0	12.0	15.0	8.0	8.0
Ammonium Laureth Sulfate	4.0	4.0	4.0	4.0	8.0	8.0
Ammonium Xylene Sulfonate	2.2	2.2	3.0	--	--	--
Cetearyl Alcohol	1.0	1.0	0.1	0.5	1.0	1.0
Glycol Distearate	0.75	2.5	0.76	0.75	0.75	0.74
Cocamide MEA	1.0	1.5	1.0	1.0	1.0	1.0
ULTRAMULSION						
Example 11	3.0	3.0	--	--	--	--
Example 12	--	--	--	3.0	--	--
Example 13	--	--	--	--	3.0	--
Example 14	--	--	3.0	--	--	--
Example 15	--	--	--	--	--	3.0
Lauryl Trimethyl Ammonium Chloride	--	--	0.75	0.75	--	--
Tricetyl Methyl Ammonium Chloride	1.0	0.5	0.5	0.5	--	--
Tri C ₈₋₁₀ Methyl Ammonium Chloride	--	--	--	--	2.0	--
Tri C ₁₃ Amine	--	--	--	--	--	2.0
Color/Perfume/ Preservative Water	_____ qv to 100% _____					

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TABLE 6

% W/W

EXAMPLE No.	24	25	26	27	28
Component					
NH ₄ C ₁₂₋₁₄ Alkyl Sulfate	--	16.0	8.0	16.0	8.0
NH ₄ C ₁₂₋₁₄ Alkyl Ether Sulfate	--	--	8.0	--	8.0
TEA C ₁₂₋₁₄ Alkyl Sulfate	18.2	--	--	--	--
Cocamide MEA	3.0	1.0	3.0	1.5	1.0
Cetearyl Alcohol	--	1.0	--	--	1.0
Ethylene Glycol Distearate	--	0.75	--	--	0.75
Sodium Hydroxide (50%)	0.6	0.01	--	--	--
ULTRAMULSION					
Example 3	2.0	--	1.9	--	--
Example 4	--	3.5	--	--	--
Example 6	--	--	--	2.0	2.0
Water/Perfume/Preservative/ Color	_____ qv to 100% _____				

EXAMPLE 29
Furniture Polish - Aerosol

Component A:	% W/W
Mineral Spirits	60.0
Lemon Oil	20.0
Carnauba Wax	14.0
Walnut Oil	3.0
ULTRAMULSION:	
Example 5	3.0
Aerosol:	
A-(above)	35.0
A-31 (isobutene)	65.0

EXAMPLE 30
Powdered Cement Sealer

Component	% W/W
Silicon Dioxide	16.0
Calcium Hydroxide	8.0
Portland Cement	60.0
Titanium Dioxide	10.0
ULTRAMULSION:	
Example 4	6.0

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EXAMPLE 31
Wall Primer

Component	% W/W
Water	66.0
Vinyl Polymer	36.0
TiO ₂	4.0
Kaolin	3.0
ULTRAMULSION:	
Example 3	2.0

EXAMPLE 32
in-Door Wall Paint

Component	% W/W
Water	50.0
Vinyl Polymer	18.0
Styrene-Acrylic Copolymer	13.0
TiO ₂	4.0
Calcium Carbonate	5.0
2-Ethoxy Butanol	2.0
Ethylene Glycol	4.0
ULTRAMULSION:	
Example 1	4.0

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WHAT IS CLAIMED IS:

1. A product selected from the group consisting of paints and coatings wherein said product contains an aqueous-free ULTRAMULSION dispersion of a silicone in a surfactant wherein:

- a. the silicone is insoluble in said surfactant, has a viscosity up to about 4 million cs, and a particle size from between about 0.5 and about 10 microns.
- b. the surfactant to silicone ratio in the ULTRAMULSION dispersion is from between about 400:1 and about 1:1; and the surfactant has an orienting effect on the silicone,
- c. the ULTRAMULSION dispersion forms stable dispersions in aqueous containing paint and coating products, and
- d. said product exhibits enhanced substantivity to substrates while the dispersed silicone phase of said ULTRAMULSION dispersion functions as a reservoir for various lipid soluble and lipid dispersible paint and coating additives.

2. A product according to claim 1, wherein said ULTRAMULSION dispersions comprises a surfactant selected from the group consisting of anionic, amphoteric, zwitterionic and nonionic surfactants and a polydimethylsiloxane wherein:

- a. said polydimethylsiloxane has the chemical composition $(\text{CH}_3)_3\text{SiO}[\text{SiO}(\text{CH}_3)_2]_n\text{Si}(\text{CH}_3)_3$, wherein n is a whole number;
- b. the viscosity of the polydimethylsiloxane ranges from between about 2.5 million and about 4 million cs;
- c. the particle size of most of the polydimethylsiloxane in the ULTRAMULSION dispersion is from between about 0.5 and about 10 microns;
- d. from between about 80% and 95% of said polydimethylsiloxane particles in the ULTRAMULSION are from between about 1 and about 10 microns;
- e. the ratio of surfactant to polydimethylsiloxane is from between about

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400:1 and about 1:2; and

- f. the ULTRAMULSION dispersion as dispersed in a water based products is stable.
3. A method of manufacturing ULTRAMULSION dispersions suitable for paint and coating products as described in claim 1 comprising, heating said surfactant and silicone mixture in a heated, stirred vessel substantially free from water, followed by subjecting said mixture to high shear dispersion.
4. A method according to claim 3, wherein the heated vessel is provided with an inert head of gas.
5. A method according to claim 3, wherein said high shear dispersing means is fitted with a small orifice.
6. A method according to claim 3 wherein said high shear dispersing means is an ultrasonication means.
7. A stable aqueous based paint product containing dispersed therein an ULTRAMULSION dispersion comprising a surfactant and a polydimethylsiloxane insoluble in said surfactant wherein:
 - a. said polydimethylsiloxane has the chemical composition $(\text{CH}_3)_3\text{SiO}[\text{SiO}(\text{CH}_3)_2]_n\text{Si}(\text{CH}_3)_3$, wherein n is a whole number;
 - b. the viscosity of the polydimethylsiloxane ranges from between about 2.5 million and about 4 million cs;
 - c. the particle size of most of the polydimethylsiloxane in the ULTRAMULSION dispersion is from between about 0.5 and about 10 microns;
 - d. from between about 80% and 95% of said polydimethylsiloxane particles in the ULTRAMULSION dispersions are from between about 1 and about 10 microns;
 - e. the ratio of surfactant to polydimethylsiloxane is from between about 400:1 and about 1:2; and
 - f. the ULTRAMULSION dispersion when dispersed in a water based paint is stable.
8. A paint product according to claim 1, wherein the ratio of said surfactant to said silicone is 9:1 and 90% of the silicone particles are from between

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about 1 and 3 microns.

9. A paint product according to claim 1, wherein the ratio of said surfactant to said silicone is 2:1 and about 100% of the silicone dispersion is less than 10 microns.

10. A paint product according to claim 1, wherein the ratio of said surfactant to said silicone is 1:1 and the silicone particles in said ULTRAMULSION dispersion are less than 10 microns.

11. An aqueous based coating containing an ULTRAMULSION dispersion comprising a surfactant and poly-dimethylsiloxane insoluble in said surfactant wherein:

- a. said polydimethylsiloxane has the chemical composition $(\text{CH}_3)_3\text{SiO}[\text{SiO}(\text{CH}_3)_2]_n\text{Si}(\text{CH}_3)_3$, wherein n is a whole number;
- b. the viscosity of the polydimethylsiloxane ranges from between about 2.5 million and about 4 million cs;
- c. the particle size of most of the polydimethylsiloxane in the ULTRAMULSION dispersion is from between about 0.5 and about 10 microns;
- d. from between about 80% and 95% of said polydimethylsiloxane particles in the ULTRAMULSION dispersions are from between about 1 and about 10 microns;
- e. the ratio of surfactant to polydimethylsiloxane is from between about 400:1 and about 1:2; and
- f. the ULTRAMULSION dispersion when dispersed in said water based coating is stable.

12. A coating product according to claim 1, wherein the surfactant is selected from the group consisting of, flowable liquids of varying viscosities, pastes, prills and cast solids.

13. A paint according to claim 7, wherein the ratio of surfactant to polydimethylsiloxane is 1:1 and at least 80% of the polydimethylsiloxane dispersed particles are between 1 and 9 microns.

14. A paint according to claim 7, wherein the ratio of surfactant to polydimethylsiloxane is 9:1 and about 90% of the polydimethylsiloxane dispersed

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particles are between 1 and 3 microns.

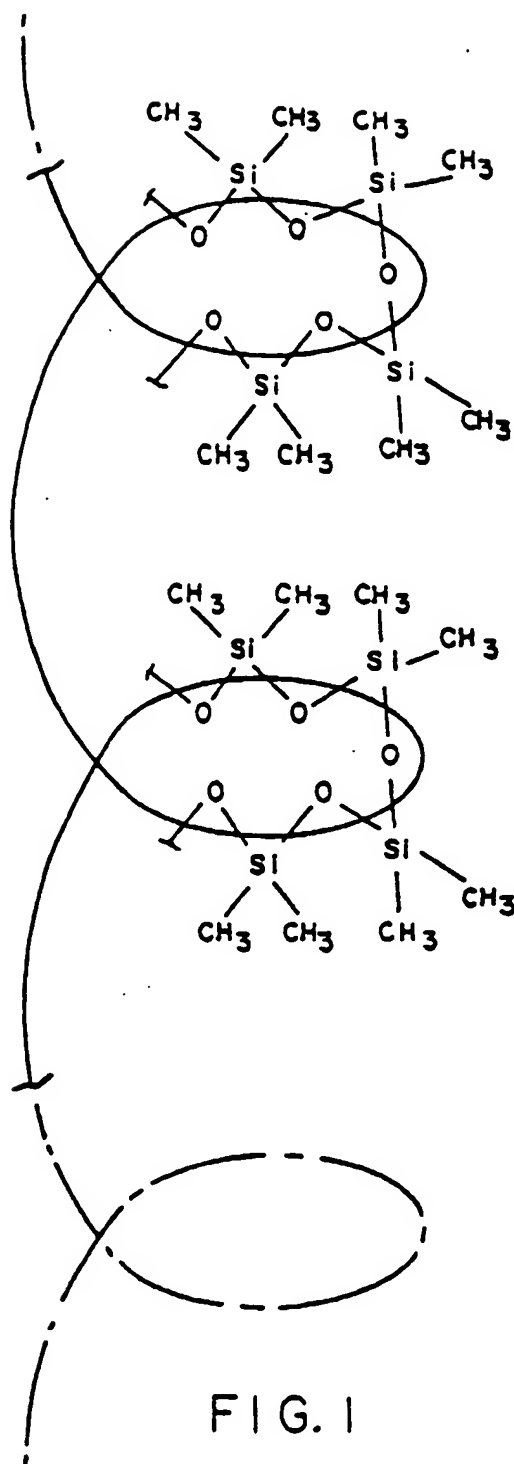
15. A paint according to claim 7, wherein the ratio of surfactant to polydimethylsiloxane is 2:1 and about 90% of the polydimethylsiloxane dispersed particles are between 1 and 3 microns.

16. A paint according to claim 7, wherein the ratio of surfactant to polydimethylsiloxane is 4:1 and about 90% of the polydimethylsiloxane dispersed particles are between 1 and 9 microns.

17. A paint according to claim 7, wherein the ratio of surfactant to polydimethylsiloxane is 9.5 : 0.5 and about 100% of the polydimethylsiloxane dispersed particles are between 1 and 9 microns.

18. A paint according to claim 7, wherein the polydimethylsiloxane has a viscosity of 2.5 million cs and the surfactant is a solid at room temperature.

1/3



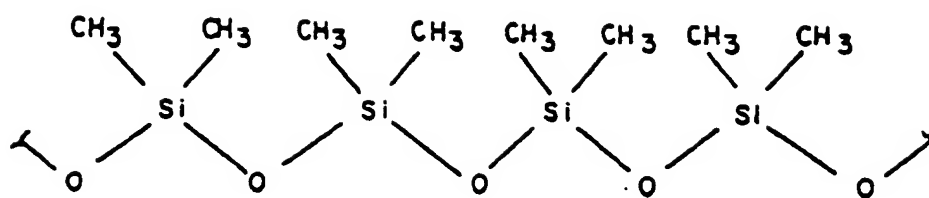


FIG. 2

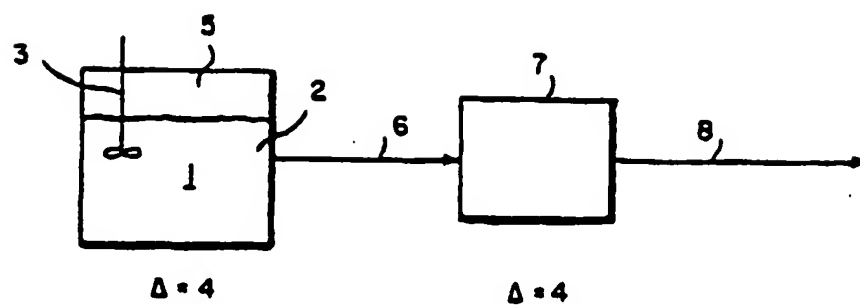


FIG. 3

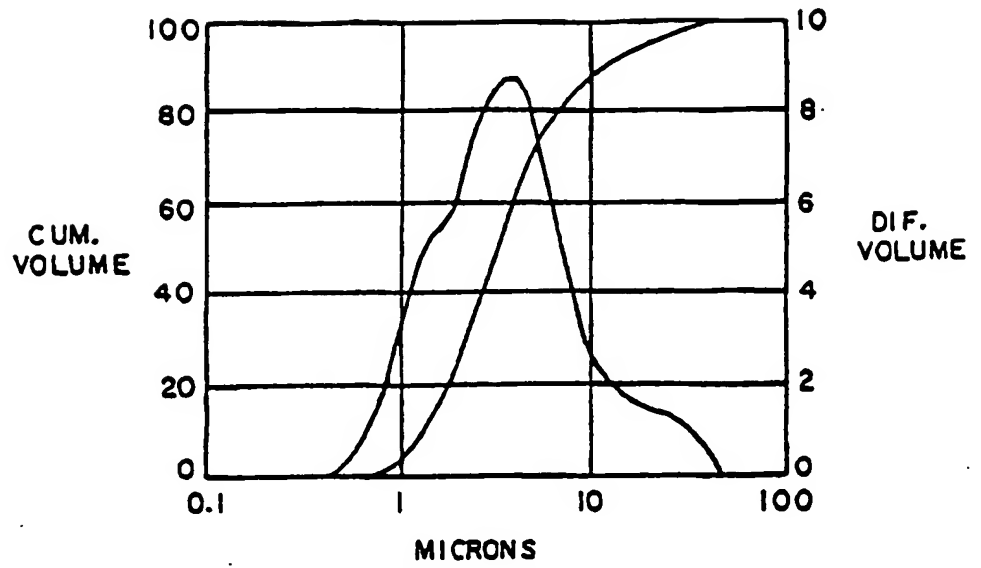


FIG. 4

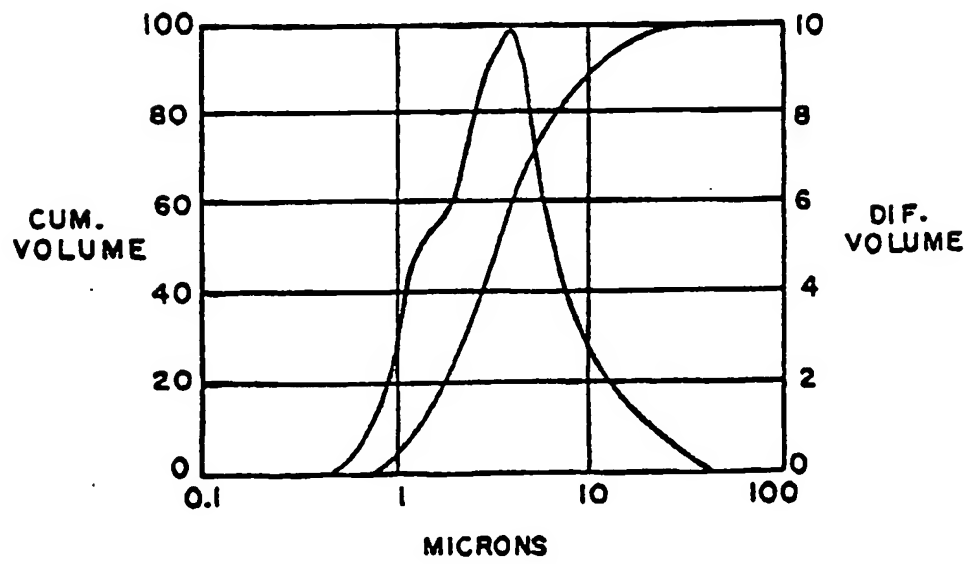


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/09197

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B01J 13/00; B23B 7/28, 7/34

US CL : 252/308, 312, 314; 106/38.22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/308, 312, 314; 106/38.22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN WPIDS

search terms: ultramulsion#, siloxane#, pluronic#, poloxamer#

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	WO, A, 95/11746 (WHITEHILL ORAL TECHNOLOGIES, INC.) 04 May 1995, see entire document, particularly abstract, claims and page 3, lines 20 et sequa.	1, 3-6, 8-10, 12 ----- 2, 7, 11, 13-18
X	US, A, 5,284,648 (WHITE et al.) 08 February 1994, Examples; claims, particularly claim 1; column 7, line 24; column 14, lines 10-14.	1 & 8
X	US, A, 2,826,551 (GEEN) 11 March 1958, Examples 2 and 1; column 2, lines 63-68 and claims.	1-2 & 7-18

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A* document defining the general state of the art which is not considered to be part of particular relevance	* X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* E* earlier document published on or after the international filing date	* Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* A*	document member of the same patent family
* O* document referring to an oral disclosure, use, exhibition or other means		
* P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

27 AUGUST 1996

Date of mailing of the international search report

1 8 SEP 1996

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/09197

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,165,913 (HILL et al.) 24 November 1992, Examples; column 19, lines 58-60; column 26, lines 59 et sequa.	1, 3, 9, 10 & 12
X	US, A, 4,780,245 (BURKE et al.) 25 October 1988, Abstract;	1
—	Examples; claims and column 5, lines 23-25.	—
A		2-18